Studies on Replacement of Phosphate Builders in Laundry Detergents Using Radiolabeled Soils[1]

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ABSTRACT

The fabric detergency performance of systems containing different types of surfactants and several builders of reduced phosphate content has been compared using a radiolabeled sebum-clay soil. Use of this soil allows quantitative measurement of both sebum and clay removal from soiled swatches, generally cotton and permanent press Dacron-cotton. One study compared alkylbenzene sulfonate (LAS), alcohol sulfate (AS), alcohol ethoxysulfate (AEOS) and alcohol ethoxylate (AEO) as surfactants in formulations containing from 0-45% sodium tripolyphosphate (STPP). Especially under hard water conditions, the AEO and AEOS considerably outperform the LAS and AS at equal use concentrations and are less sensitive to phosphate reduction. Tests with cotton swatches soiled with five different carbon black-oil mixtures generally rank the surfactants in the same order, although individual responses of the cloths vary considerably. A further study compares the effect of replacing STPP with sodium nitrilotriacetate (NTA) in formulations containing varying amounts of AEO or LAS. Detergency improves significantly with increasing surfactant concentration, particularly with AEO, and declines as builder strength is reduced. AEO exceeds LAS considerably in performance under the test conditions even at relatively high concentrations of LAS. Another study compares the performance of AEO and LAS at equal concentrations in formulations containing a variety of

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TABLE I

Sebum Composition

Component	Weight %	Label
Lubricating oil	25	^{3}H
Tristearin	10	^{3}H
Arachis oil	20	---
Stearic acid	15	^{14}C
Oleic acid	15	^{14}C
Octadecanol	8	^{14}C
Cholesterol	7	^{14}C

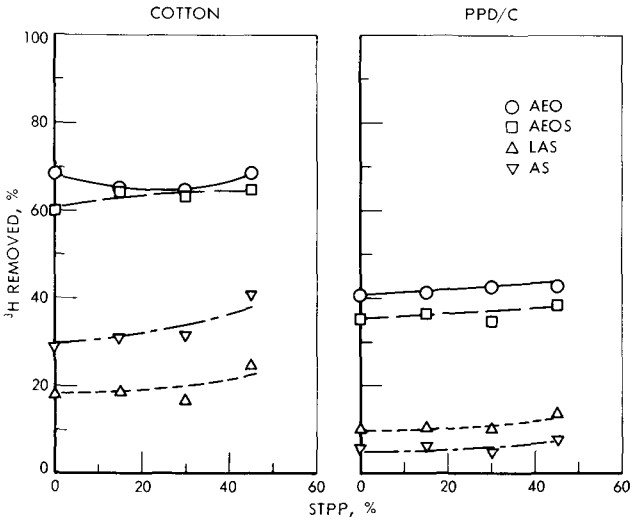

FIG. 1. Effect of STPP content on nonpolar (^{3}H) sebum removal: 120 F, 250 ppm, 1.0 g product/liter, 15% surfactant.

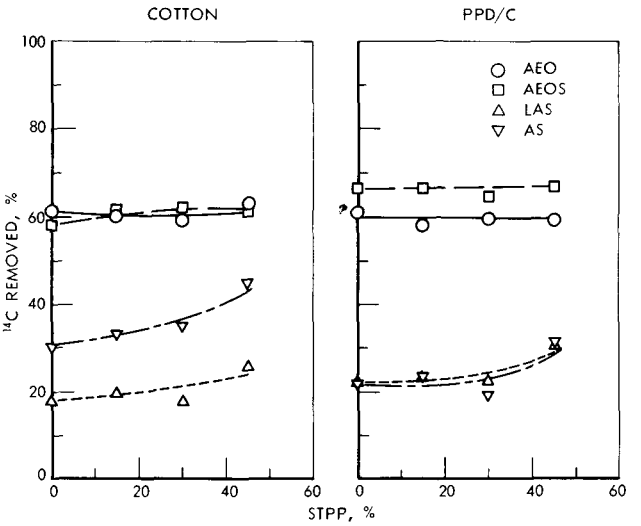

FIG. 2. Effect of STPP content on polar (^{14}C) sebum removal: 120 F, 250 ppm, 15% surfactant, 1.0 g product/liter.

TABLE II

Test Conditions: Comparison of Typical Surfactants

Product formulation, wt %	A	B	C	D
Surfactant	15	15	15	15
STPP	45	30	15	0
Sodium silicate	7	7	7	7
CMC	0.5	0.5	0.5	0.5
Sodium sulfate	q.s.[a]	q.s.	q.s.	q.s.
Potential sequestration capacity, as ppm of wash liquor	122	81	41	0
Washing conditions				
Product concentration		1.0 g/liter		
Water hardness, as $CaCO_3$		250 ppm		
Temperature		120 F		

[a]Quantity sufficient.

TABLE III

Test Conditions: Effect of Surfactant Concentration and Builder Composition

Condition	Test 1	2	3	4
Product formulations, wt %				
Surfactant, AEO or LAS		10 to 30		
Builder[a]	A	B[b]	C[b]	D[b]
STPP	45	20	20	0
NTA	0	15	10	15
Potential sequestration capacity, as ppm of wash liquor	122	109	91	55
Washing conditions				
Product concentration		1.0 g/liter		
Water hardness, as $CaCO_3$		150 ppm		
pH of NTA wash liquors		70 F	120 F	
Initial		9.9-10.2	9.4-9.6	
After wash		9.5- 9.7	9.1-9.3	

[a]Plus 8% sodium silicate, 0.5% CMC, quantity sufficient sodium sulfate.

[b]Plus 3% sodium carbonate.

builders. AEO is generally superior to LAS in removing both sebum and clay soils and is less sensitive to builders and water hardness. The builders generally rank in this order: STPP > NTA = citrate > carbonate > sulfate.

INTRODUCTION

A number of research programs are being carried out in these laboratories as a contribution to the very large effort in the detergent industry toward elimination of phosphate builders from laundry products. Past approaches which have been considered include the use of surfactants insensitive to hard water (1,2), various polymeric (3,4) or other (5) sequestrants, or combined surfactant-builders (6). At high concentration levels, tallow-based surfactants have been tested with a variety of builders (7). As in the work to be reported, the use of increased concentrations of conventional surfactants has been suggested (8). The present paper reports some of our studies in which a detergency test method recently developed in these laboratories (9), using radiolabeled sebum and clay soils, is employed to assess the effectiveness of the various formulations.

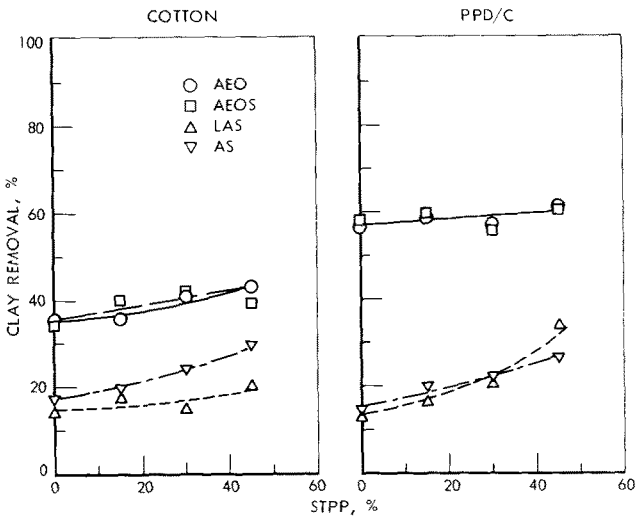

FIG. 3. Effect of STPP content on clay removal: 120 F, 250 ppm, 15% surfactant, 1.0 g product/liter.

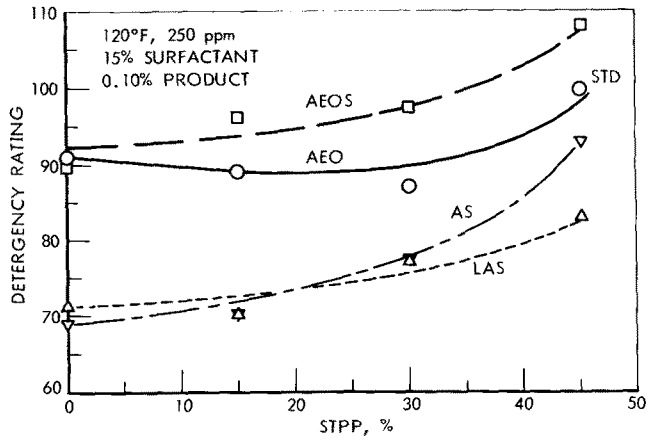

FIG. 4. Effect of surfactant type and STPP content on detergency rating using carbon-soiled cotton test cloths: average ratings with UST, TFI, FDS, EMPA and ACH cloths; AEO with 45% STPP = 100.

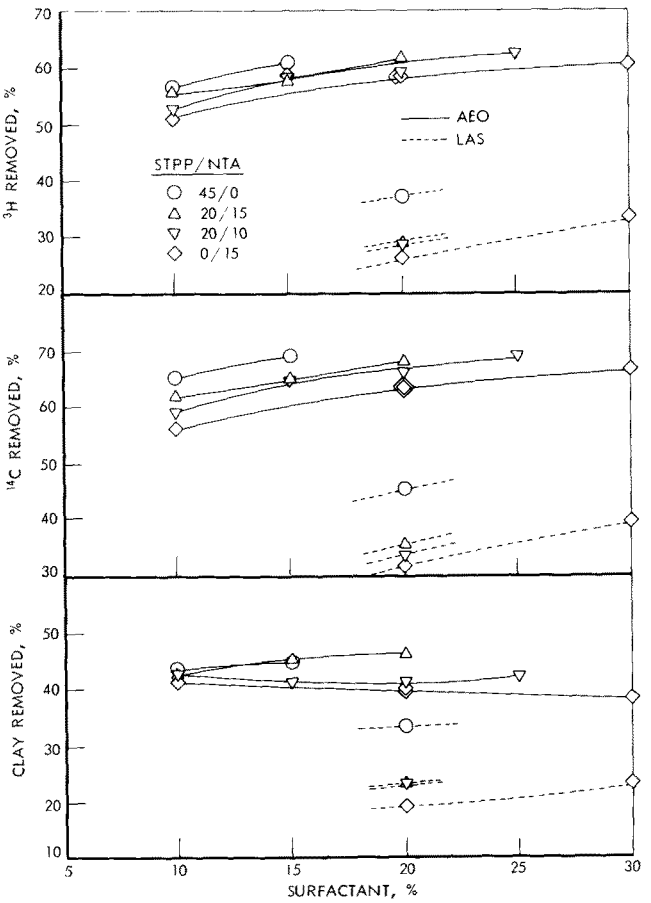

FIG. 5. Effect of surfactant concentration and builder composition on soil removal from cotton at 120 F: 150 ppm, 1.0 g product/liter.

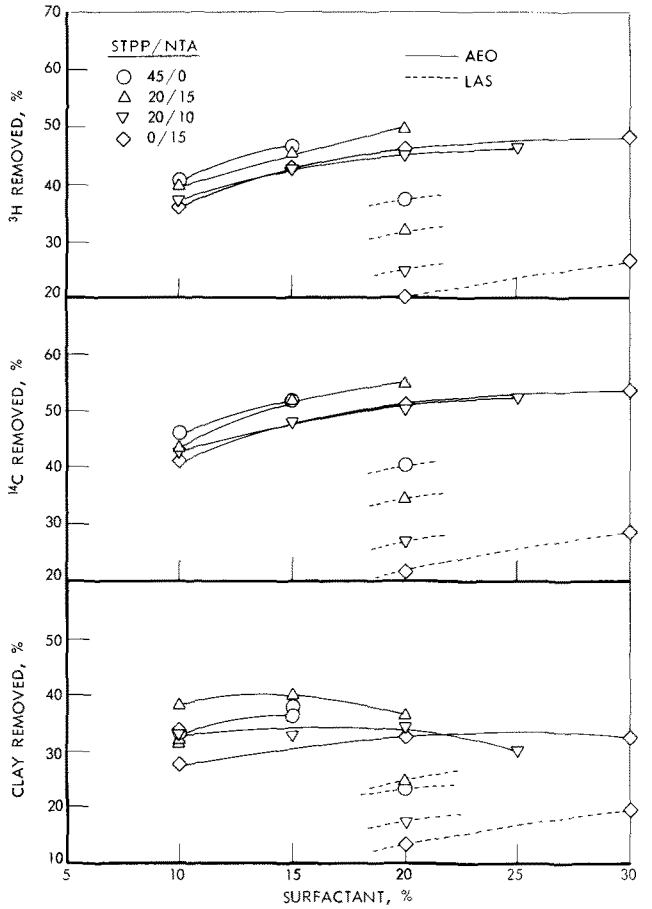

FIG. 6. Effect of surfactant concentration and builder composition on soil removal from cotton at 70 F: 150 ppm, 1.0 g product/liter.

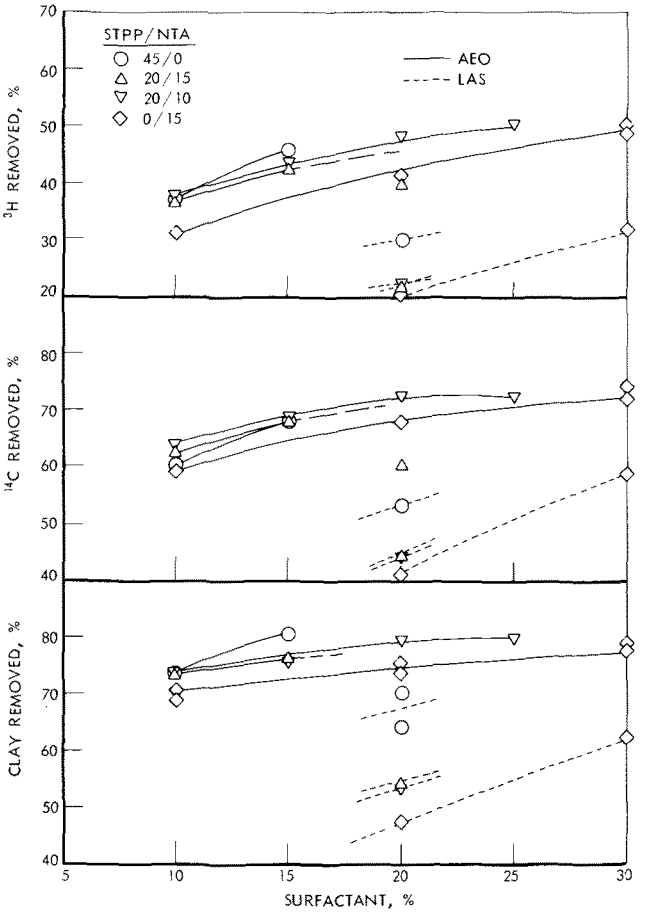

FIG. 7. Effect of surfactant concentration and builder composition on soil removal from PPD/C at 120 F: 150 ppm, 1.0 g product/liter.

One of these studies compares the sensitivity to water hardness of a number of anionic and nonionic surfactants in detergents with decreasing phosphate content. A second study compares the effects of increasing surfactant concentration on performance of low builder content detergents based on alkylbenzene sulfonate (LAS) and primary alcohol ethoxylate (AEO) surfactants. A third study compares a variety of candidate nonphosphate builders in LAS and AEO detergents.

The radiolabeled detergency performance test method allows quantitative determination of the removal of nonpolar sebum soil, polar sebum soil and clay soil individually from the soiled cloth swatches in the washing operation.

EXPERIMENTAL PROCEDURES

Four 10 cm square soiled swatches of a given type were washed in a Terg-o-Tometer for 10 min at 100 rpm in 500

TABLE IV

Test Conditions: Effect of Different Builders

Formulation	Per cent	Potential hardness removal,[a] $CaCO_3$, ppm
Surfactant (AEO or LAS)	15	---
Sodium silicate (RU)	7	---
CMC	1	---
Sodium sulfate	37	---
Builder	40	---
Builder Candidates		
1. STPP	40	163
2. NTA $\cdot H_2O$	25	137
Sodium carbonate	5	71
Sodium sulfate	10	0
3. Sodium citrate $\cdot 2H_2O$	40	204[b]
4. Sodium carbonate	40	565
5. Sodium sulfate	40	0
Washing conditions		
Temperature	120 F	
Water hardness, as $CaCO_3$	150 and 300 ppm	
Product concentration	1.5 g/liter	

[a]By sequestration or precipitation of the hardness in the wash liquor containing 0.15% product. Expressed as hardness of the wash water.

[b]Probably not effective at pH 9-10.

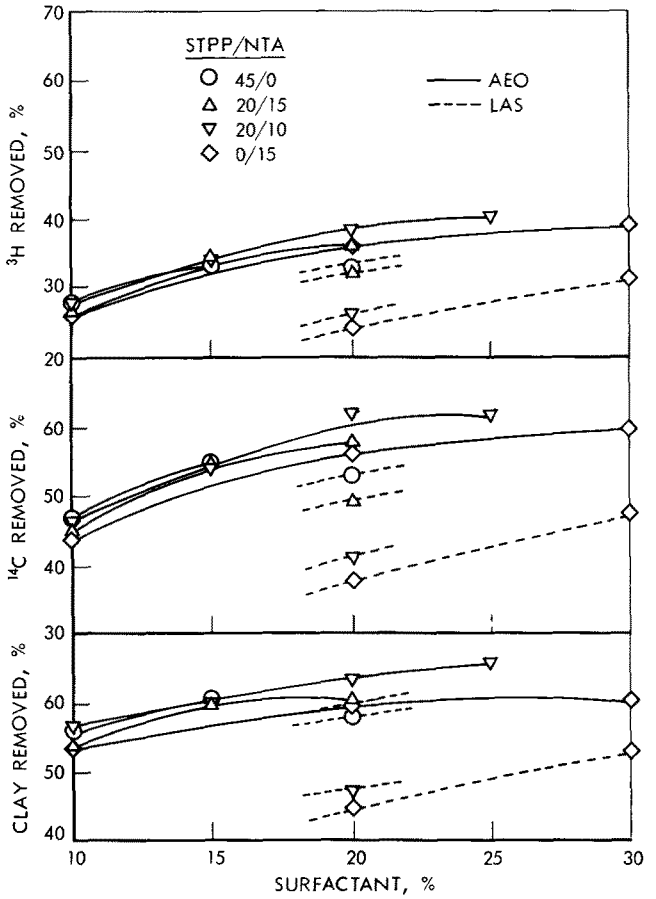

FIG. 8. Effect of surfactant concentration and builder composition on soil removal from PPD/C at 70 F: 150 ppm, 1.0 g product/liter.

ml of wash liquor and rinsed by hand in 105 ml of distilled water. Water hardness, expressed as ppm $CaCO_3$, was derived from a stock solution of calcium and magnesium chlorides, having a 60:40 Ca^{++}/Mg^{++} molar ratio. Bleached cotton sheeting and a 65:35 Dacron® 54-cotton blend with permanent press finish (Testfabrics, Inc., New York, Style Numbers 405 and 7406 WRL, respectively) were used for the radiolabeled soils. In a few tests, purchased cotton swatches soiled with various oily carbon black mixtures were used, each type of swatch being washed separately. Reflectance measurements and computer calculations were performed according to the method of Illman et al. (10). The cloths and their sources are as follows: U.S. Testing Company (UST), Hoboken, N.J.; Foster D. Snell Research, Inc. (FDS), New York (this cloth is no longer available); ACH Fiber Service, Inc., Boston Mass.; Testfabrics (TFI) and EMPA 101, Testfabrics, Inc., New York.

Radiolabeled clay, 4-5 mg/swatch, was applied from an aqueous suspension in hard water using the method of Gordon and Shebs (9). After gamma-ray counting the swatches in groups of four to determine the initial clay content, 28 mg of doubly labeled sebum (11) having the composition in Table I was applied to each swatch from benzene solution. Nonpolar sebum components are labeled with tritium, polar components with carbon-14. After air drying, the swatches were washed with the detergents under test and then gamma-ray counted to determine the residual clay content. Aliquots of the combined wash and rinse waters were counted in a three-channel liquid scintillation counter to determine the tritium and carbon-14 contents of the sebum removed, as described by Shebs and Gordon (11). Computer methods were used to calculate the per cent of each soil component removed.

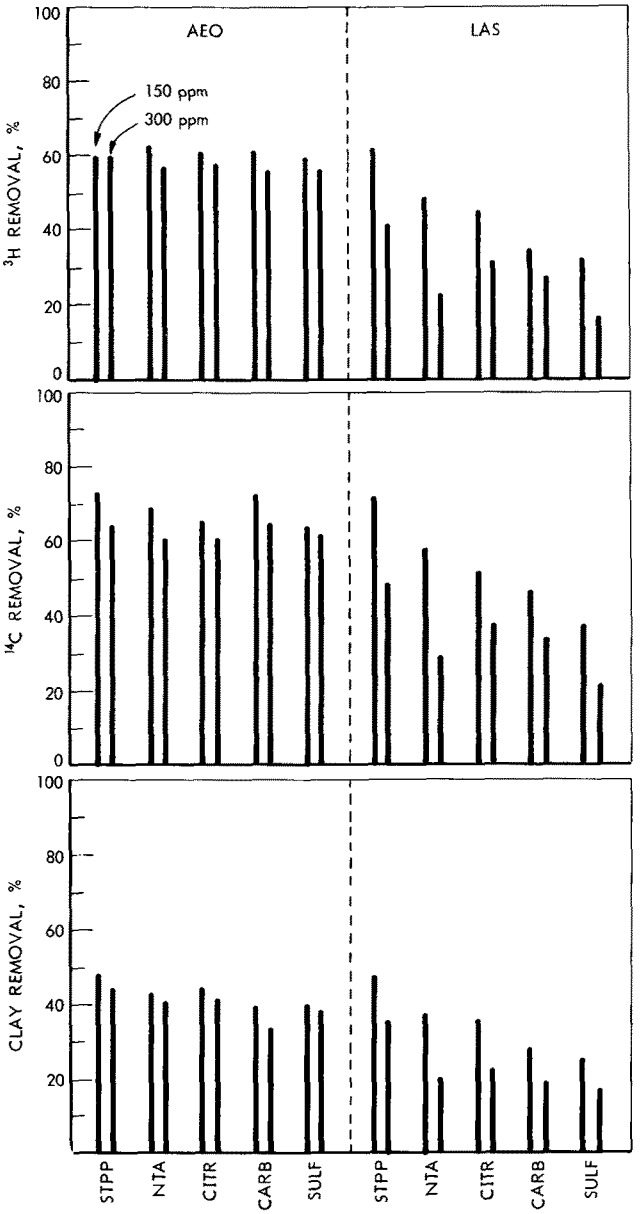

FIG. 9. Soil removal from cotton with various builders.

RESULTS AND DISCUSSION

Effects of Phosphate Reduction With Typical Surfactants

A comparison was made of the detergency performance of four surfactants in formulations of reduced phosphate content. The surfactants were a linear primary alcohol ethoxylate (based on NEODOL® Detergent Alcohols) in the C_{12}-C_{15} range with 9-11 ethoxylate groups (AEO), the sodium salt of a C_{16}-C_{18} linear primary alcohol sulfate (AS), a C_{13} alkylbenzene sulfonate (LAS), and a linear primary alcohol ethoxysulfate (based on NEODOL® Detergent Alcohols) in the C_{12}-C_{15} range with three ethoxylate groups (AEOS). Formulations and washing conditions are shown in Table II. At the selected levels of detergent concentration and water hardness, assuming a 1:1 molar ratio of STPP/Ca^{++} or Mg^{++}, only about half of the hardness was sequestered even at the highest phosphate content, thereby emphasizing the hardness sensitivity of the surfactants.

Figures 1-3 show nonpolar and polar sebum and clay removal from cotton and from permanent press Dacron-cotton (PP D/C) fabrics. It is immediately apparent that AEO and AEOS are quite comparable, and they consider-

ably exceed LAS and AS in performance under the selected conditions.

Throughout all of the work with the tagged soils, it can be seen that the cotton and permanent press Dacron-cotton fabrics differ in their washability. As was discussed in an earlier paper (12), the tritium-labeled sebum is more readily removed from cotton than from PP D/C while the reverse is true with the clay soil.

Tests using five conventional oily carbon black soil test cloths showed a considerable variation in response. However UST, FDS and ACH cloth, and the five fabric average results shown in Figure 4, generally agree with the tagged sebum clay results.

Effect of Surfactant Concentration and Builder Composition

Tests in which the effect of concentration of AEO and LAS surfactants in formulations where STPP was replaced in whole or in part with sodium nitrilotriacetate monohydrate (NTA) were carried out under the conditions shown in Table III. All builders contained 8% of sodium silicate and 0.5% carboxymethyl cellulose (CMC) and, if NTA was present, 3% sodium carbonate to maintain an effective pH level. The water hardness was reduced to a more typical level of 150 ppm, but the product concentration was such that even with the best builder, no more than 122 ppm was sequestered.

Figures 5-8 show detergency performance for sebum-clay soiled cotton and PP D/C fabrics at both 120 F and 70 F washing temperatures. It is again apparent, with incomplete sequestration of the water hardness, that AEO considerably out-performs LAS. It further appears that a modest increase of some 50% in AEO concentration in the formulations deficient in builder restores detergency performance to that of the high builder level. Increased concentration is less effective with LAS.

Effect of Different Builders

Sodium citrate, sodium carbonate and NTA builders were compared to STPP and sodium sulfate (blank) in formulations containing AEO or LAS surfactants under conditions shown in Table IV. Fixed amounts of surfactant, sodium silicate and CMC were used, together with 40% of the builder candidate. The NTA builder formulation contained only 25% NTA plus 5% sodium carbonate and 10% sodium sulfate. Also shown is the potential of each builder candidate to remove hardness from the wash water by either sequestration or precipitation, assuming stoichiometric relationships. Figures 9 and 10 show the mean soil removal values from duplicate washings of cotton and PP D/C, respectively. An analysis of variance was performed, and although the detailed statistical results are not presented here, all statements made are valid at the 95% level.

The formulations based on AEO are better than those based on LAS with all nonphosphate builders. Generally the poorer the builder, the better is the performance of AEO compared to LAS. With all builders AEO is less sensitive to the builder and to the water hardness than LAS.

Considering all levels of surfactant, hardness and cloth, the ranking of the builders is as follows for each soil: clay and nonpolar sebum: STPP > sodium citrate = NTA > sodium carbonate > sodium sulfate; and polar sebum: STPP > NTA = sodium citrate = sodium carbonate > sodium sulfate (NTA > sodium carbonate). Thus at the 40% level, sodium carbonate is inferior to STPP, sodium citrate (except with the carbon-14 labeled polar sebum soil) and 25% NTA. However the rankings are governed largely by behavior with LAS; with AEO sodium carbonate performs as well as STPP in sebum removal.

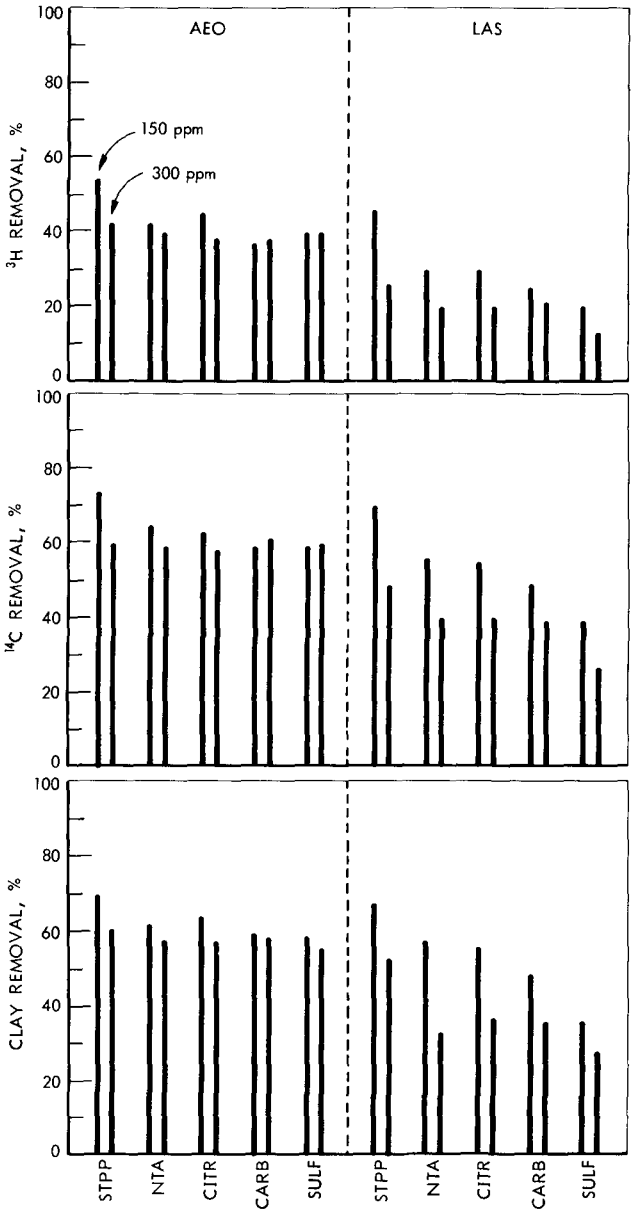

FIG. 10. Soil removal from permanent press Dacron-cotton with various builders.

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